Statically and Dynamically Stable Lithium-Sulfur Batteries

ARUMUGAM MANTHIRAM

Materials Science and Engineering Program

The University of Texas at Austin

June 8, 2017

Project ID #: ES284

OVERVIEW

Timeline

- Project start date: October 2015
- Project end date: September 2018
- 50 % complete

Budget

- Total project funding
  - DOE: $ 891K
- Funding received in FY 2016
  - $ 297K
- Funding for FY 2017
  - $ 297K

Barriers

- Barriers
  - Energy and power densities
  - Cycle life
  - Self-discharge and shelf-life
- Targets
  - High-capacity, high-loading sulfur cathodes with high energy density, long cycle life, and low self-discharge

Partners

- None officially

RELEVANCE

Overall Project Objective

- Develop statically and dynamically stable lithium-sulfur batteries
  - Develop a polysulfide (PS)-filter-coated separator
  - Develop Li-S batteries with high sulfur content and high sulfur loading
  - Optimize and develop advanced lithium-sulfur cell designs

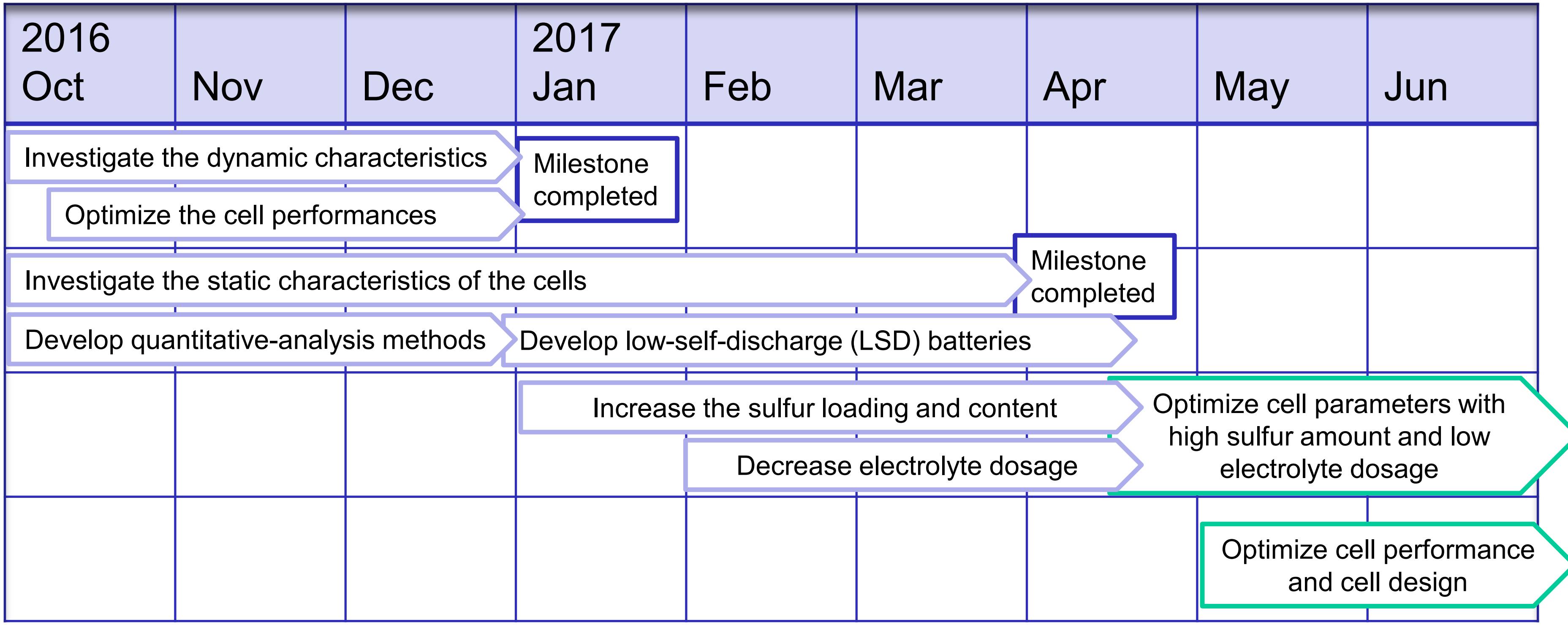
Objectives for Year 2

- Development of Li-S cells with (i) high sulfur content and loading and (ii) dynamically and statically stable battery performances
  - Improve dynamic electrochemical performance (cycle life) (high sulfur utilization, low capacity fade, and long cycle life)
  - Improve static electrochemical performance (shelf-life) (low self-discharge rate and high cyclable capacity after storage)
  - Achieve high sulfur content and loading
  - Optimize Li-S cells with high sulfur content/loading and stable cyclability

MILESTONES

Month/Year	Milestone	Status
December 2016	Technical: Analyze and improve the dynamic electrochemical performances of Li-S cells by inserting PS-filter-coated separators	Completed
March 2017	Technical: Analyze and improve the static electrochemical performances of Li-S cells by inserting PS-filter-coated separators	Completed
June 2017	Technical: Increase the sulfur loading of the cells	Ongoing
September 2017	Go/No-go: Fabricate cells with high sulfur content/loading and good electrochemical stability	Ongoing

APPROACH



- **Milestones and Go/No-go decision for Year 2 (FY 2017)**
  - The Milestones on the dynamic and static performances have been completed (marked as *Milestone completed* above)
  - The Go/No-go decision on the development of Li-S cells with high sulfur content and loading as well as dynamically and statically stable battery performances will be made after the cell measurements and optimization are finished

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

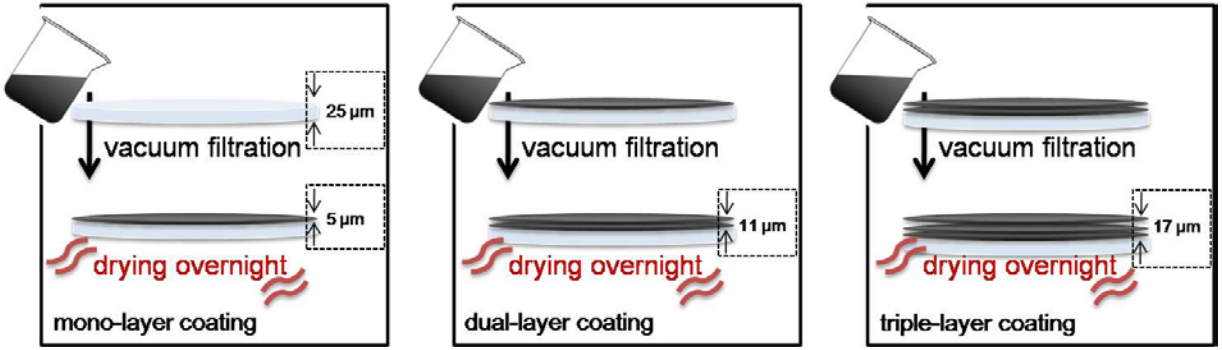
- (Y2Q1) Realized Li-S cells with enhanced dynamic electrochemical stability (long cycle life) with the following features:
  - (i) high sulfur utilization (> 80 %), and
  - (ii) steady and long life (500 cycles) during cycling
- Investigation of high-loading sulfur cathodes (4.0 mg cm^{-2} or higher) reveals that significant changes arise in the battery chemistry/performances upon going from low-loading sulfur cathodes to high-loading sulfur cathodes

- (Y2Q2) Realized Li-S cells with enhanced static electrochemical stability (low self-discharge (LSD)) with the following features:
  - (i) low self-discharge rate (< 0.5% per day) during resting
  - (ii) the longest shelf-life of over one year
  - (iii) quantitative-analysis tools for studying self-discharge
- Long-term self-discharge investigation evidences that a short-term study (within 15 days) cannot reflect the accurate self-discharge effect

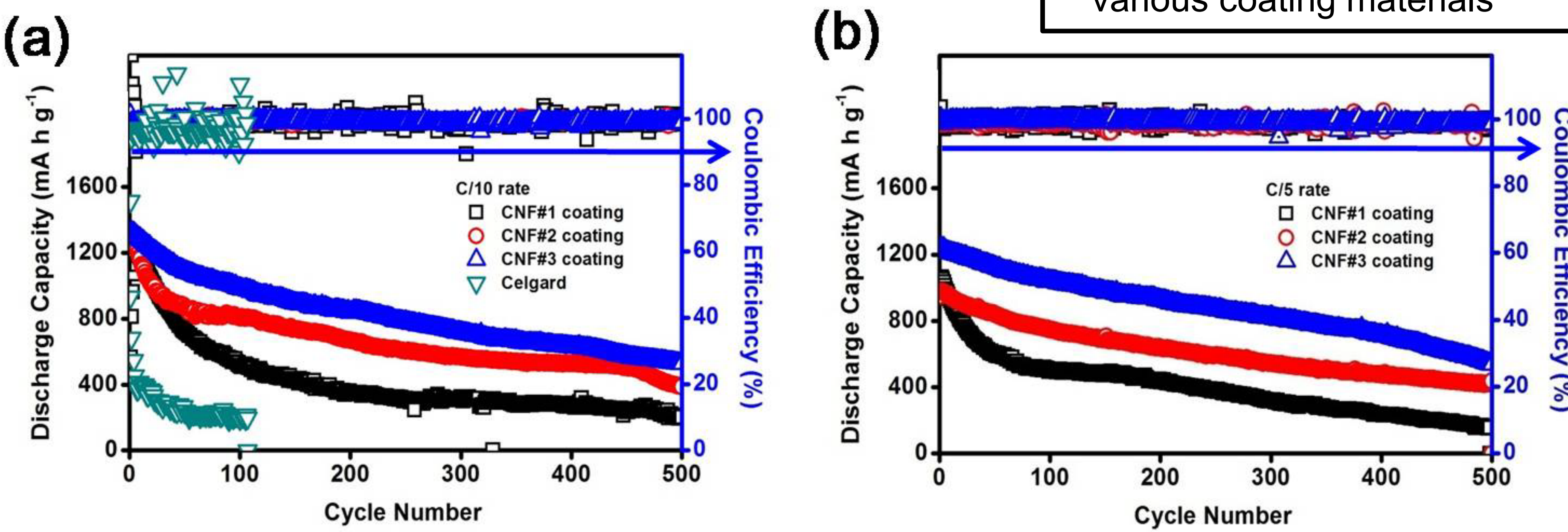
MATERIALS CHEMISTRY DATABASE

- (Y1Q1 – Y1Q4) The materials chemistry database developed (i) benefits the design of advanced coating techniques (layer-by-layer (LBL) coating) for coating carbons on the polymer Celgard separators and (ii) optimizes the PS-filter coatings with lower mass loadings, thinner coating, and better polysulfide-trapping performances
- (Y1Q1 – Y1Q4) The materials chemistry database developed indicates that the cells fabricated with a porous carbon coating on the separator give high electrochemical performances, but the promising cell performance happens only when the cells have a superabundant electrolyte dosage
- (Y1Q3 – Y2Q2) According to the understanding gained in Y1, we have designed cells with higher sulfur loading and lower electrolyte dosage by employing nonporous carbon substrates and specially designed cathode architectures

DYNAMIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH NONPOROUS CARBON NANOFIBER (CNF)-COATED SEPARATORS



- Advantages of LBL coating of carbon on the separators:
  - thin coating film
  - low coating mass
  - layered PS-filter interfaces
  - mass production with various coating materials

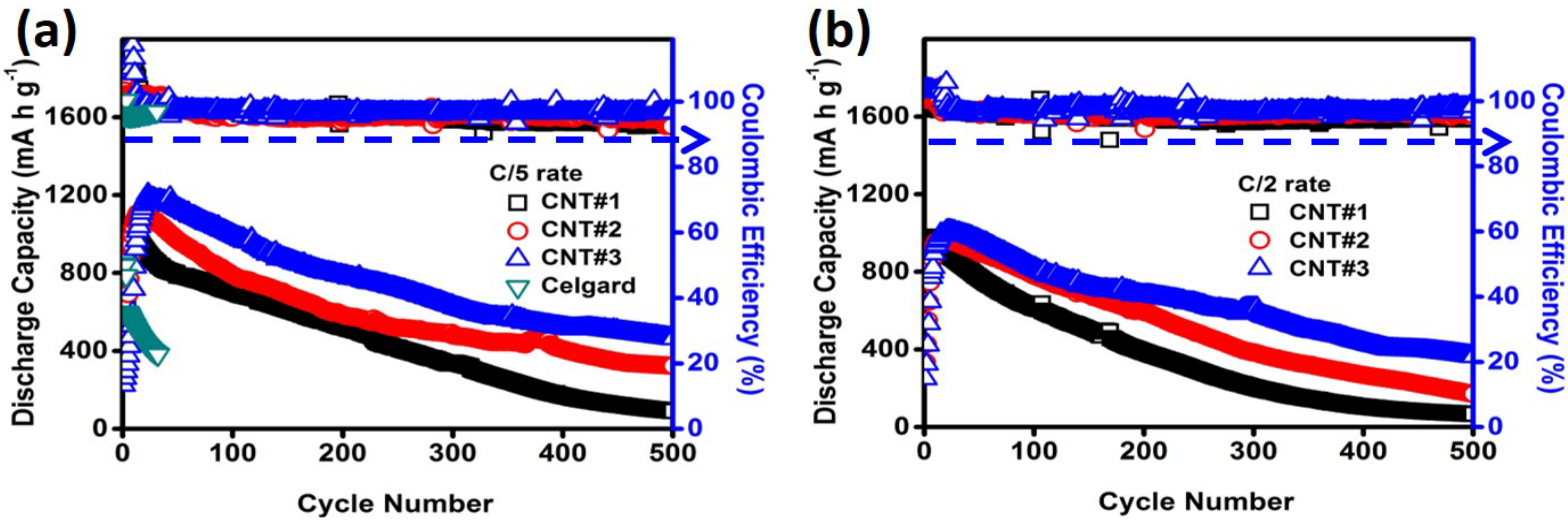


Cyclability of the cells employing LBL CNF-coated separators at (a) C/10 and (b) C/5 rate for 500 cycles

- (Y1Q4 – Y2Q1) LBL CNF-coated separators display a high sulfur utilization of 80% and an areal capacity of 4.3 mA h cm^{-2} (targeted values: 80% and 4.0 mA h cm^{-2})

S.-H. Chung and A. Manthiram, *ACS Energy Letter* (submitted)

DYNAMIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH NONPOROUS CARBON NANOTUBE (CNT)-COATED SEPARATORS

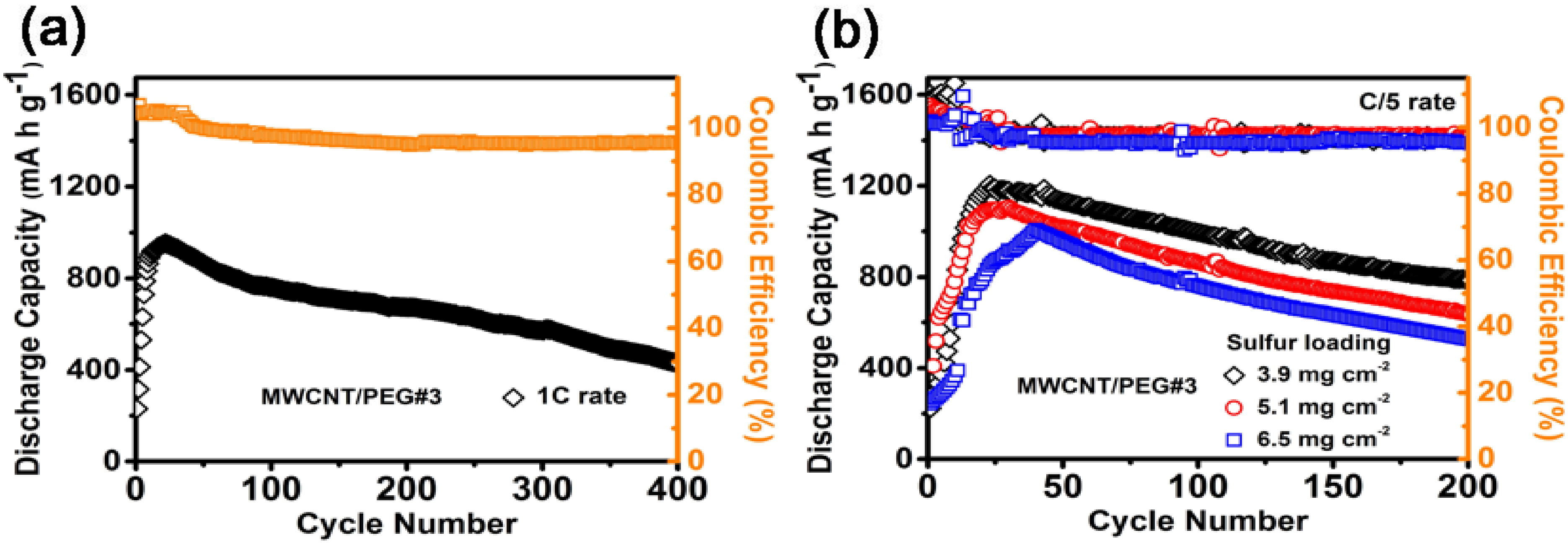


Cyclability of the cells employing LBL CNT-coated separators at (a) C/5 and (b) C/2 rates for 500 cycles

- (Y1Q4 – Y2Q1) LBL CNT-coated separators exhibit cyclability similar to CNF-coated separators, but offer better high-rate performances with lower coating mass loadings
- (Y2Q1) High-rate performances: C/5 and C/2 rates for 500 cycles (targeted value: 500 cycles)
- (Y1Q4) Light-weight coating: reducing the mass loadings from 0.1 – 0.4 mg cm^{-2} to 0.04 – 0.12 mg cm^{-2}

L. Luo, S.-H. Chung, and A. Manthiram, *Journal of Materials Chemistry A*, **4**, 16805–16811 (2016)
S.-H. Chung and A. Manthiram, *ACS Energy Letter* (submitted)

DYNAMIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH NONPOROUS CARBON NANOTUBE (CNT)-COATED SEPARATORS



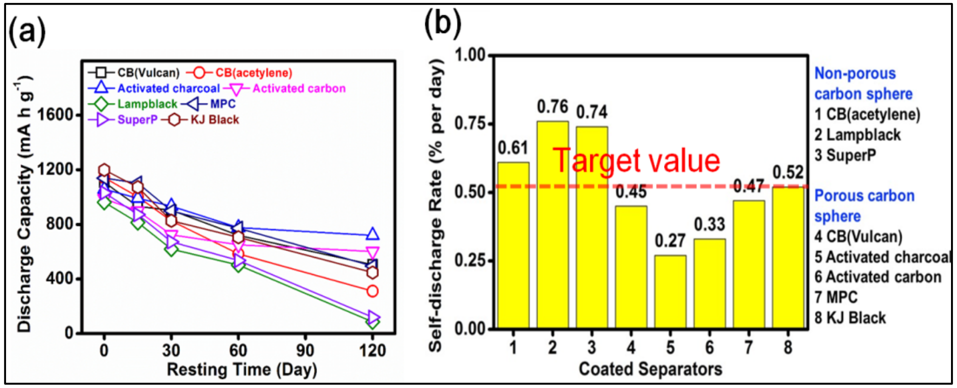
Cyclability of the cells employing LBL CNT-coated separators (a) with 3.9 mg cm^{-2} sulfur cathode at 1C rate and (b) with high-loading sulfur cathode at C/5 rate

- (Y1Q4 – Y2Q1) LBL CNT coatings facilitate fast electron transport in sulfur cathodes
- (Y1Q4 – Y2Q1) Enhanced redox kinetics enable high-loading sulfur cathodes (3.9 mg cm^{-2}) to operate smoothly at high 1C rate and allow further increase in sulfur loading up to 6.5 mg cm^{-2} (targeted value: 4.0 mA h cm^{-2})
- The positive features seen evidence that the project is on track toward building electrochemically stable Li-S cells with high-loading cathodes (Y2Q3 – Y2Q4)

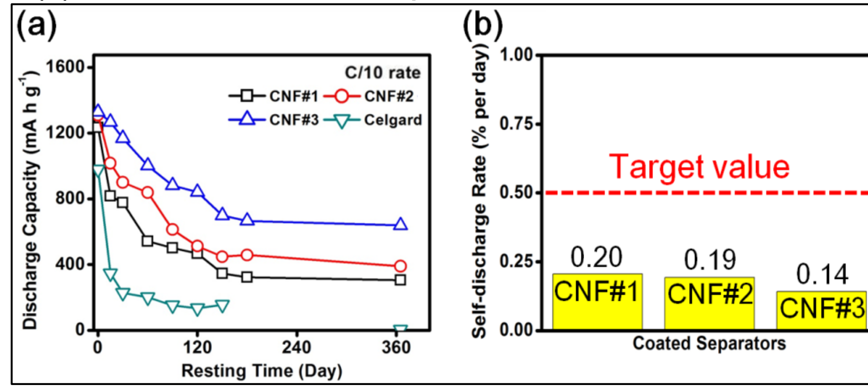
L. Luo, S.-H. Chung, and A. Manthiram, *Journal of Materials Chemistry A*, **4**, 16805–16811 (2016)

STATIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH VARIOUS CARBON-COATED SEPARATORS

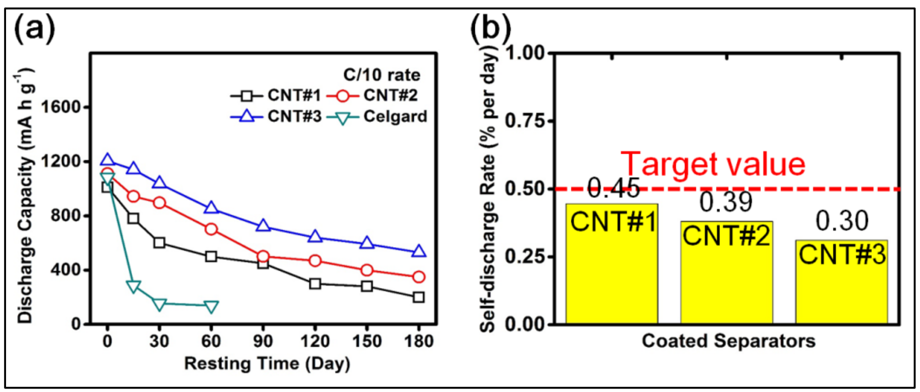
(i) Spherical carbon-coated separators



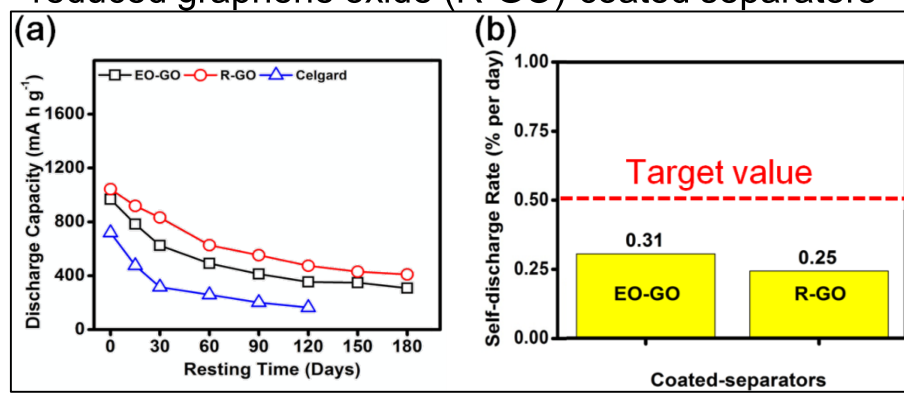
(ii) LBL CNF-coated separators



(iii) LBL CNT-coated separators



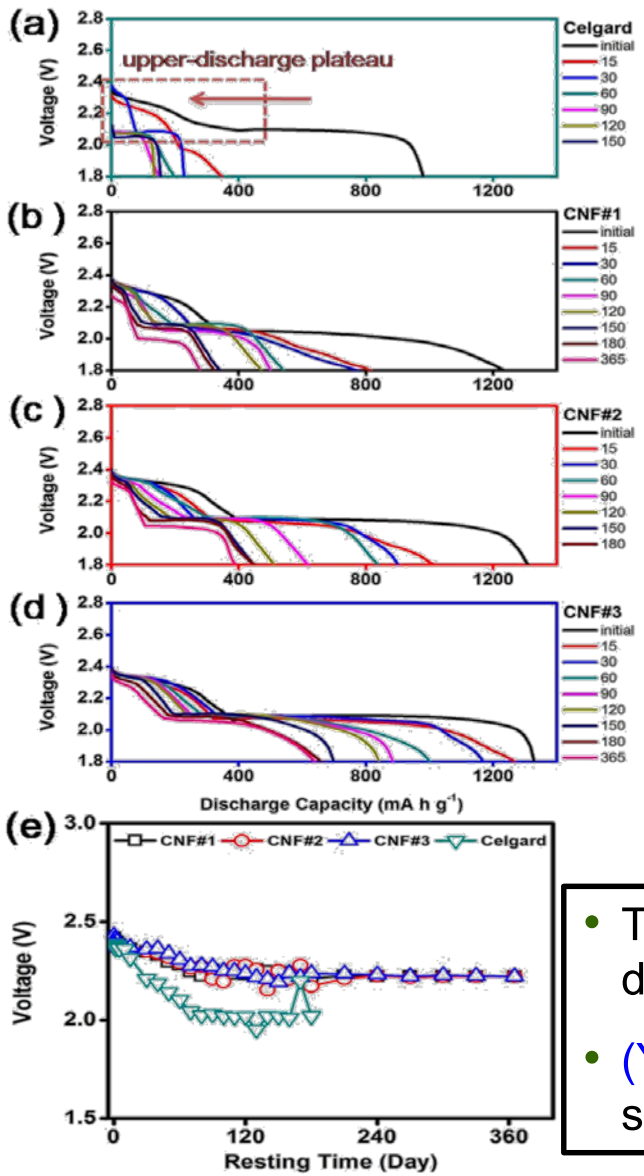
(ii) edge-oxidized graphene oxide (EO-GO) / reduced graphene oxide (R-GO)-coated separators

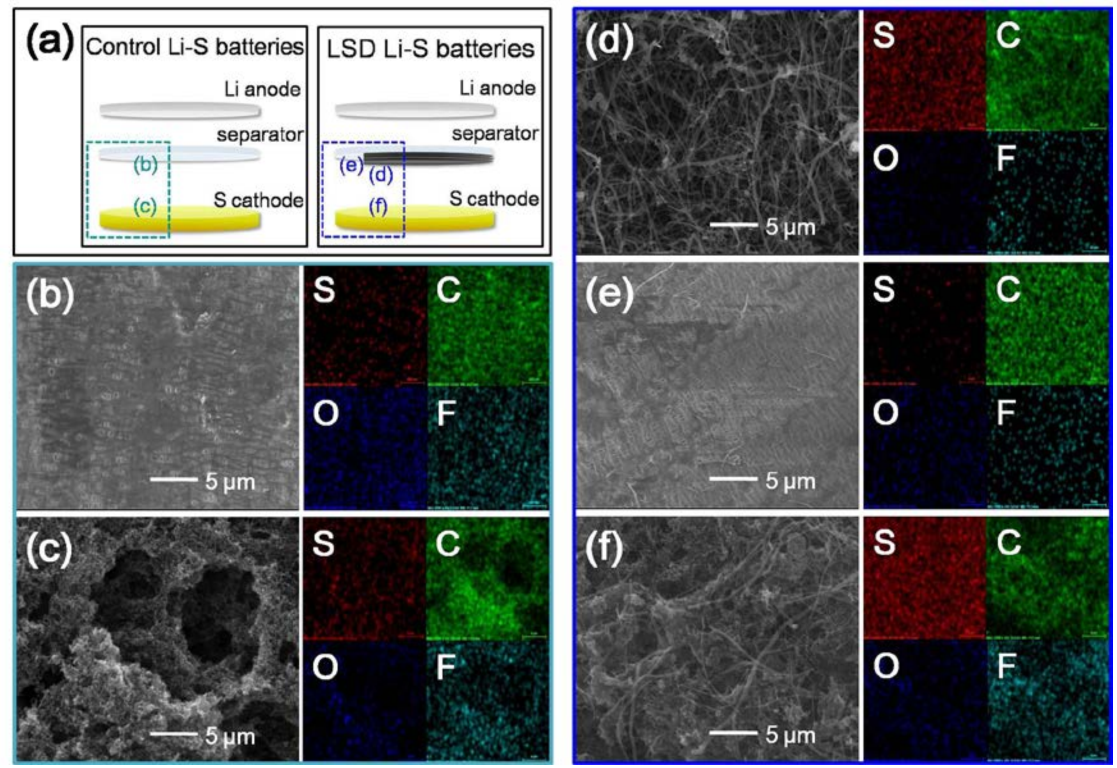


(a) Static electrochemical stability and (b) self-discharge rate of the cells with PS-filter-coated separators

- The lack of a long-term study of self-discharge effect and shelf-life of Li-S batteries causes a serious problem for making the Li-S battery technology viable
- (Y1Q3, Y2Q2) PS-filter-coated separators ensure good static electrochemical performances with (i) low self-discharge rate (< 0.5% per day) and (ii) good cycle stability

STATIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH NONPOROUS CARBON NANOFIBER (CNF)-COATED SEPARATORS

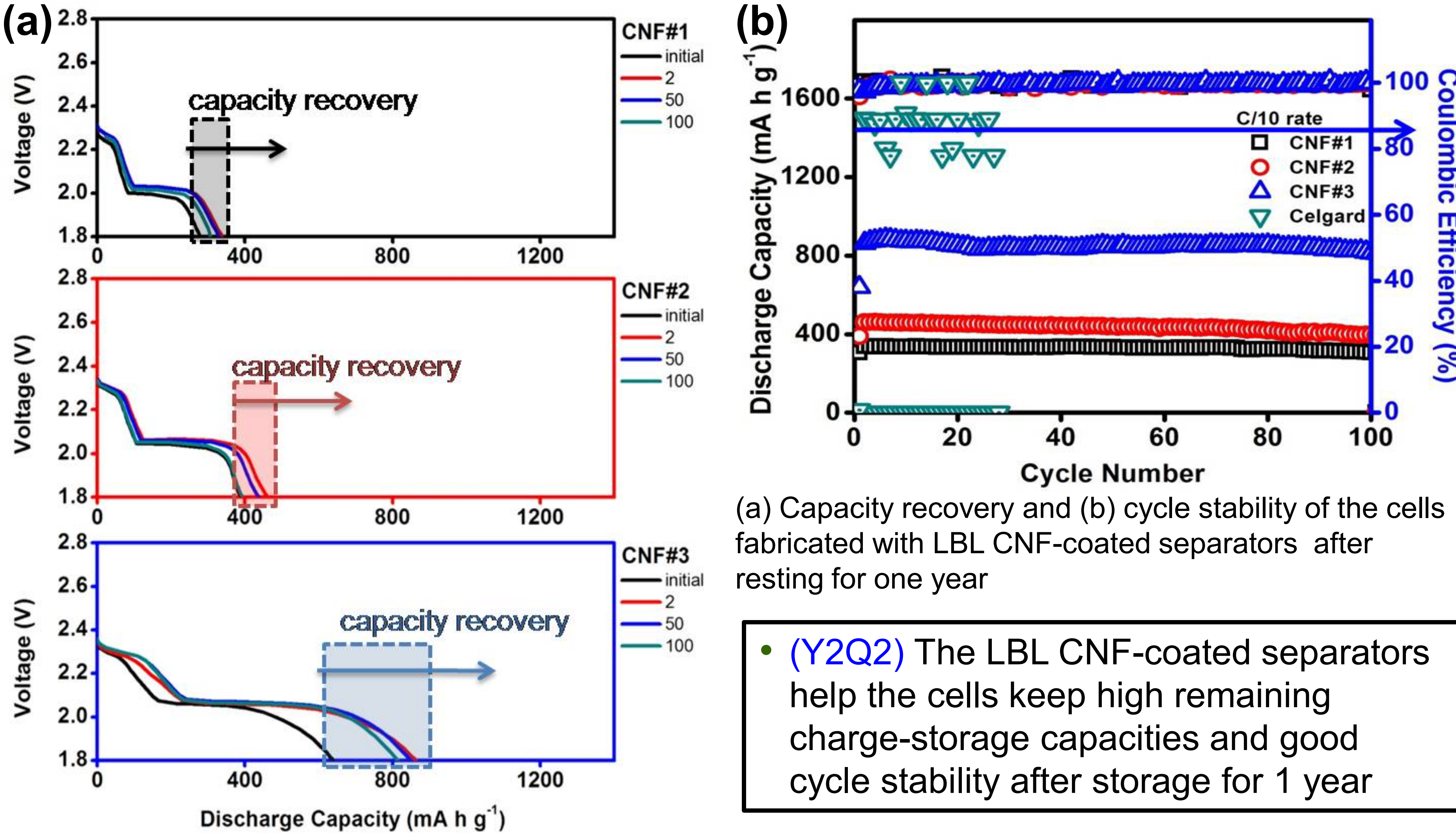




SEM inspections of the rested cells (1 year) fabricated with (a-c) conventional cell configuration and (a,d-f) LBL CNF-coated separators

- The sulfur-to-polysulfide conversion and the polysulfide dissolution cause severe self-discharge
- (Y2Q2) The use of PS-filter-coated separators suppresses polysulfide diffusion during cell resting

STATIC Li-S ELECTROCHEMISTRY: CELLS FABRICATED WITH NONPOROUS CARBON NANOFIBER (CNF)-COATED SEPARATORS

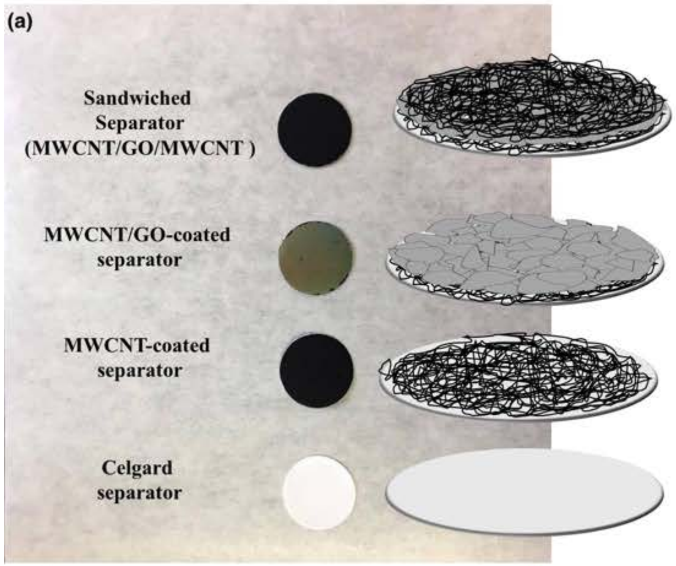


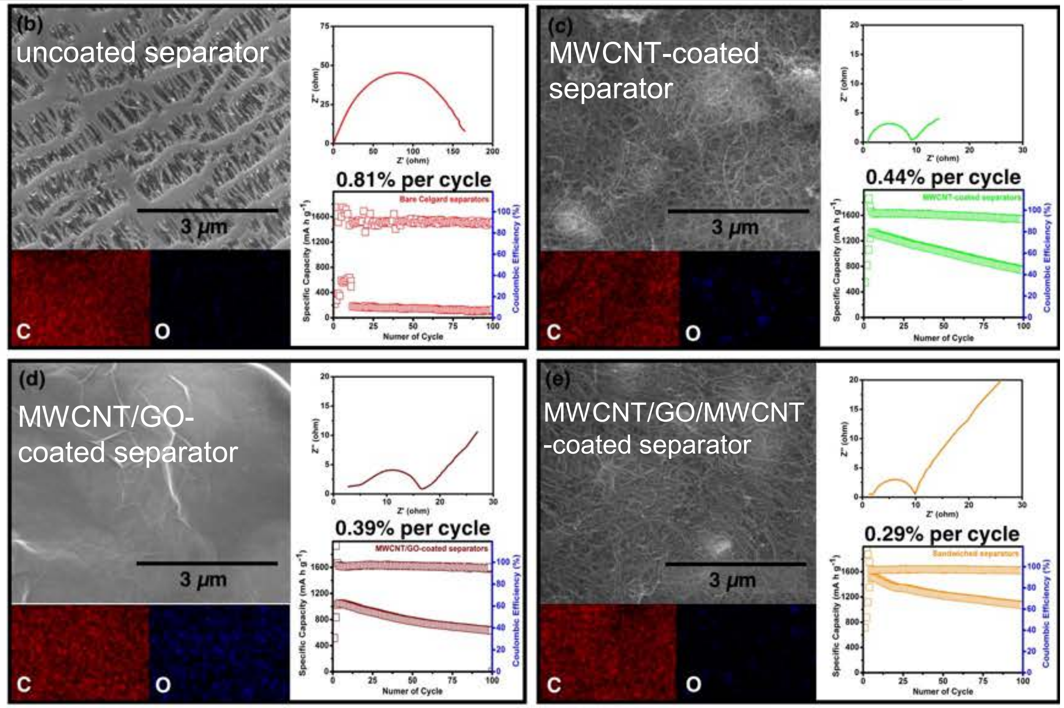
(a) Capacity recovery and (b) cycle stability of the cells fabricated with LBL CNF-coated separators after resting for one year

- (Y2Q2) The LBL CNF-coated separators help the cells keep high remaining charge-storage capacities and good cycle stability after storage for 1 year

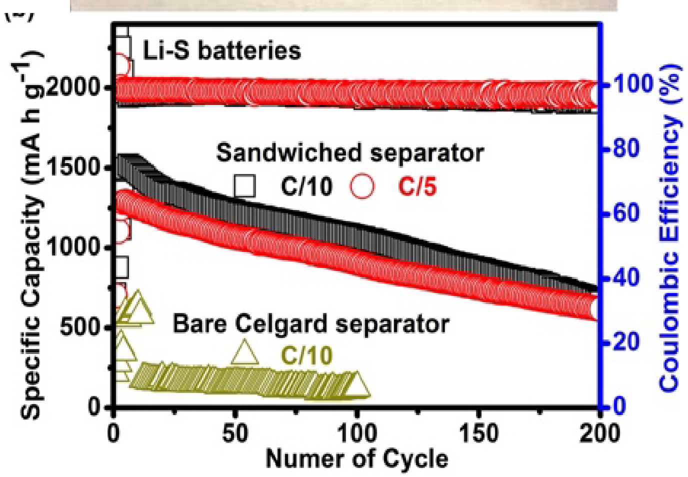
S.-H. Chung, P. Han and A. Manthiram, *Journal of Materials Chemistry A* (submitted)
S.-H. Chung and A. Manthiram, *ACS Energy Letter* (submitted)

COMPOSITE PS-FILTER-COATED SEPARATORS





(a-e) SEM and electrochemical characteristics of the coatings

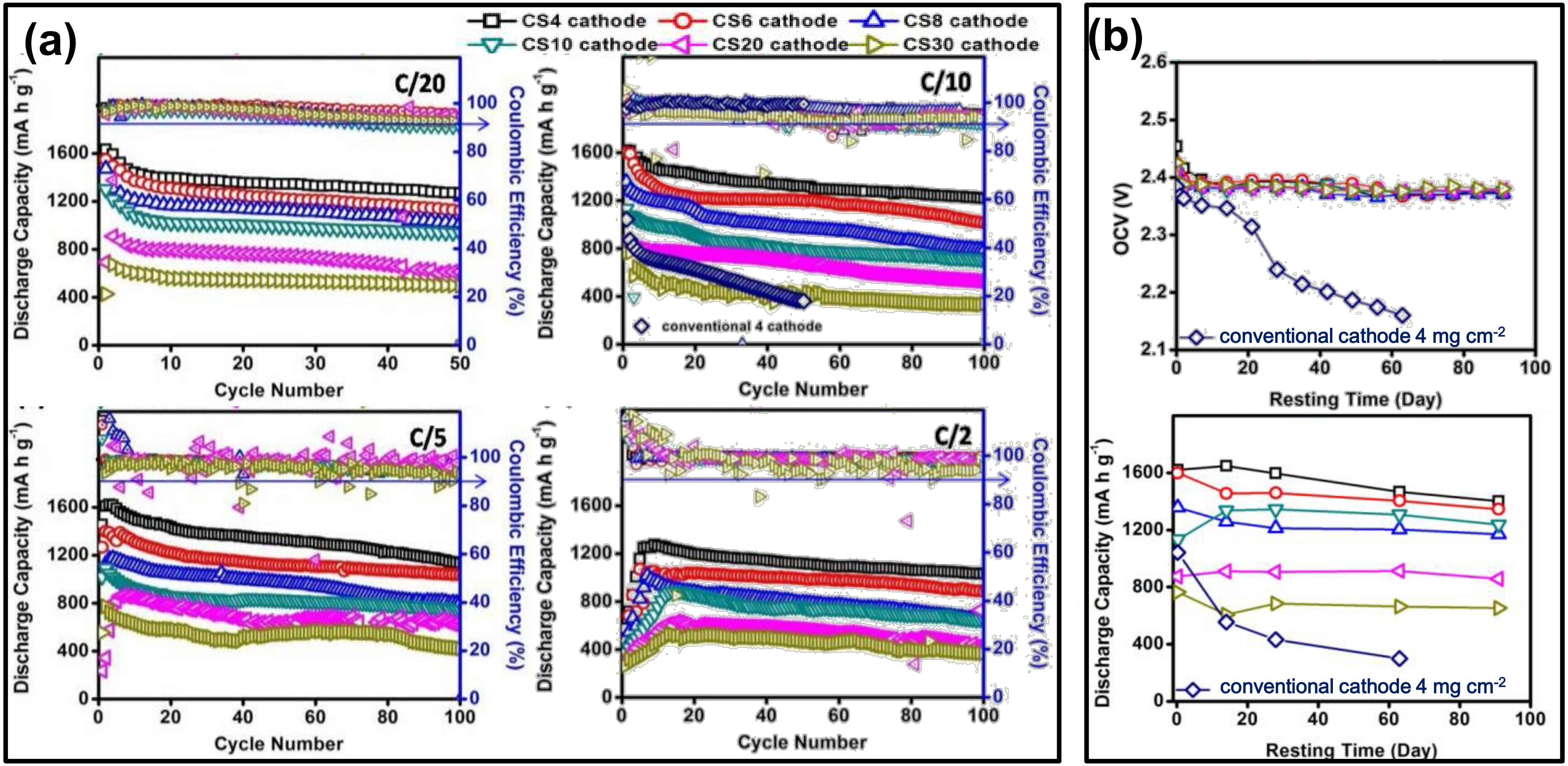


Electrochemical performances of the cells fabricated with high loading cathode and MWCNT/GO/MWCNT-coated separators

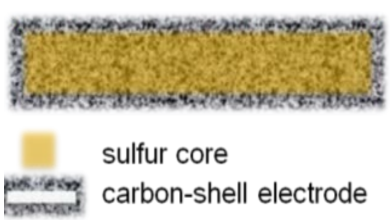
- Composited MWCNT/GO/MWCNT-coated separators integrate (i) a MWCNT upper current collector, (ii) a GO polysulfide anion-repellant layer, and (iii) a conductive MWCNT polysulfide-trapping for high-loading (7 mg/cm^2) pure sulfur cathodes (Y2Q3 – Y2Q4)

C.-H. Chang, S.-H. Chung, S. Nanda, and A. Manthiram, *Advanced Energy Material* (in preparation)

HIGH-LOADING CORE-SHELL SULFUR CATHODES



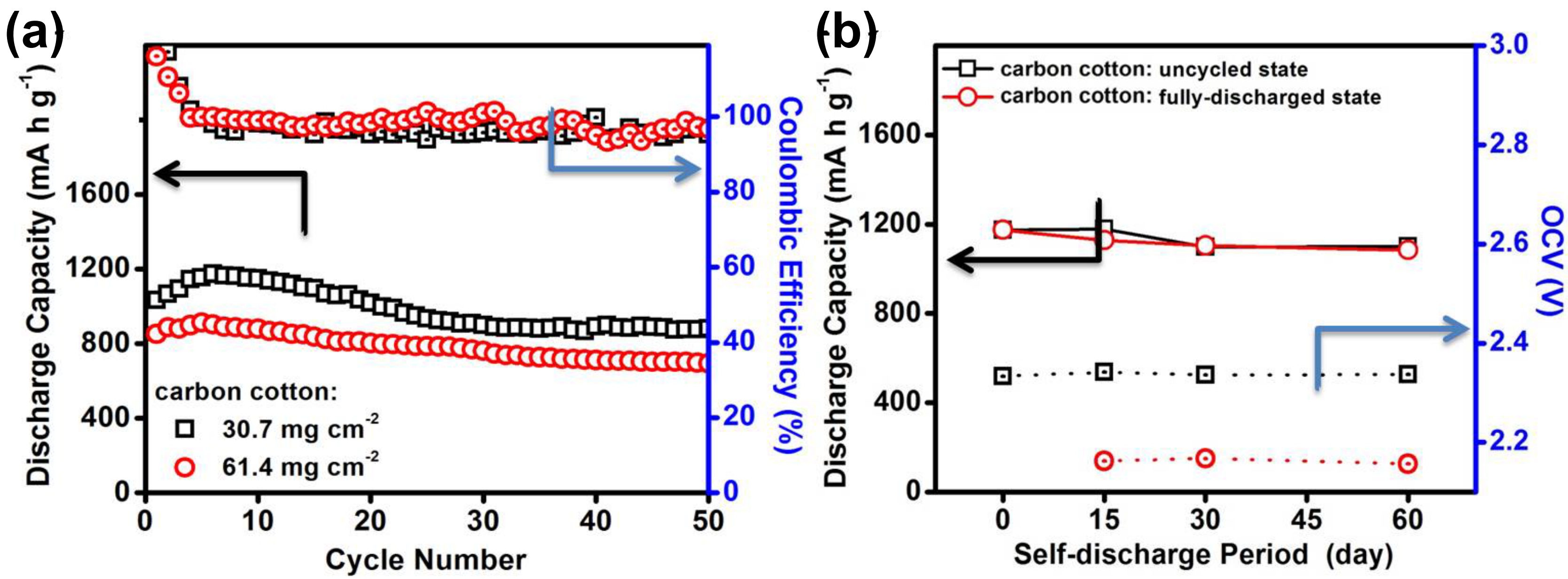
(a) Cycling performances and (b) self-discharge analyses of the cells employing core-shell cathodes



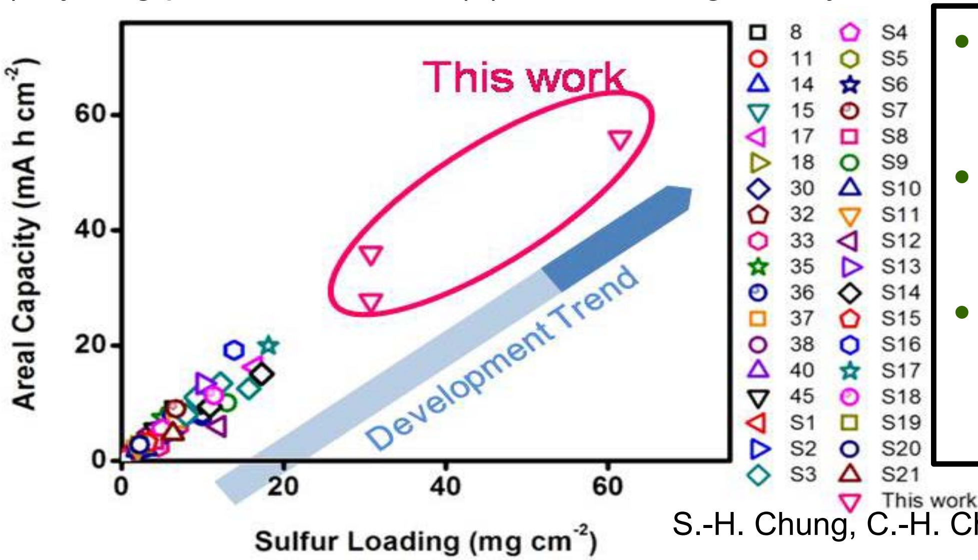
- Sulfur loading and content up to 30 mg cm^{-2} and 67 wt.% S
- Good rate capability up to C/2 and low self-discharge (Y2Q3 – Y2Q4)

S.-H. Chung, C.-H. Chang, and A. Manthiram, *Energy & Environmental Science* **9**, 3188 (2016)

HIGH-LOADING CARBON-COTTON SULFUR CATHODES



(a) Cycling performance and (b) self-discharge analysis of the cells employing carbon-cotton cathodes



- High sulfur loading/content up to 64 mg cm^{-2} and 80 wt.% S
- Low electrolyte/sulfur (E/S) ratio of 6.8
- High areal capacity of 56 mA h cm^{-2} and low self-discharge rate of 0.1% after resting for 2 months

S.-H. Chung, C.-H. Chang, and A. Manthiram, *ACS Nano* **11**, 10462 (2016)

RESPONSE TO REVIEWERS' COMMENTS

In general, the reviewers pointed out this project is sound and focused. The responses to some specific comments are provided below:

Comment: *At some point the huge volume of electrolyte needed to enable S cathodes to work has to be addressed. This reduces Wh/kg by quite a bit.*
Response: We agree with the reviewer. The commonly used nanoporous carbons and nanocomposites do need superabundant electrolytes to realize high electrochemical performance. To address this issue, we have developed a LBL coating that allows the use of nonporous carbon as high-performance coating materials in fabricating the PS-filter-coated separators. We have also presented our low-electrolyte-usage cells with the carbon-cotton cathode (electrolyte/S ratios = 6.8) in this AMR report.

Comment: *Trapping polysulfides closer to their place of origin is better than filtering at the separator.*
Response: The PS-filter-coated separators are arranged to attach directly onto the sulfur cathodes for effectively filtering the diffusing polysulfides and keeping them within the cathode region of the cell.

Comment: *Although the reviewer observed good improvement, there is still a long way to go and work on thick electrodes is just starting.*
Response: In this AMR report, we have presented high-loading sulfur cathodes (core-shell and carbon-cotton structure). Both cases have an ultrahigh sulfur loading of > 30 mg cm^{-2} and even approaching 61 mg cm^{-2}.

Comment: *It was unclear to this reviewer whether the team understands the cause of the observed capacity fade: loss of S through reactions of polysulfides at the Li-metal interface; loss of access to S due to electrical isolation; or buildup of Li-metal SEI*
Response: The capacity fade can occur due to all the factors the reviewer pointed out, but if we suppress the polysulfide migration from the cathode region as we do with our carbon-coated separators, factors 1 and 2 can be eliminated. We focus on maintaining a high utilization of sulfur during cycling through novel cathode engineering/architectures as we presented in this report with core-shell and carbon-cotton cathodes.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Dr. Gabriel Veith, Oak Ridge National Laboratory

  Thin-film deposition of air-sensitive sulfide materials and Li_2S for Li_2S-based batteries

  - pure Li_2S cathode
  - Li_2S-coated cathodes
  - ionically conducting thin films (*e.g.*, Li_2S-P_2S_5)
  - composite thin films (Li_2S and a conductive material)

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:** The Graphene oxides (GOs) are popular carbon materials used in battery research. The literature reports, however, indicate that the sole use of GOs or raw materials derived from them could not directly lead to high-performance Li-S cells. Therefore, we use composited coatings consisting of GOs.

- **Challenge/Barrier 2:** Self-discharge is a serious problem in making the Li-S battery technology practically viable. However, no long-term self-discharge data are available in the literature as it involves a time-consuming experimental process. Therefore, we are engaged in systematically assessing the self-discharge behavior by storing the cells up to 1 year as presented in this report.

PROPOSED FUTURE WORK

- FY2017
  - To address Challenge/Barrier 1: Based on the comprehensive basic study in Year 1 on major carbons used in Li-S battery research, we have selected the best GO samples for getting the necessary electrochemical data with a long cycle stability (200 cycles). Based on the preliminary results obtained, we further focus on developing the GO-coated separators as the MWCNT/GO/MWCNT-coated separators as a new composite PS-filter coating.
  - To address Challenge/Barrier 2: After locking on the coating materials, we have begun the self-discharge study. As a result, we are able to present the first long-term self-discharge study along with the low self-discharge Li-S cells in this report.
  - (Q3 July-17) Technical Milestone III: We are focusing on fabricating cells with high sulfur content/loading: cells with a sulfur content of 70 wt. % and a sulfur loading of 5 mg cm^{-2} with good electrochemical stability.
  - (Q4 Sep-17) Technical Milestone IV: We will focus on cells with high sulfur content/loading that can offer good static and dynamic stabilities with long cycle life and low self-discharge.
- FY2018
  - (Q1 Dec-17) Technical Milestone I: We will focus on PS-filter-coated separators with anode-side-protection coatings or Li-metal protection additives combined. We will introduce anode stabilization techniques for avoiding dendrite growth and internal short circuit, enhancing the safety of Li-S cells using Li-metal anodes.

Any proposed future work is subject to change based on funding levels.

SUMMARY

- The materials chemistry database and the corresponding fabrication methods developed are benefiting the development of carbon-coated separators with lightweight/thin-film carbon coating and high-performance Li-S cells (Y1)

- The enhanced dynamic and static electrochemical stability are reflected in:
  (i) high sulfur utilization (> 80 %, Y2Q1)
  (ii) steady and long cyclability (500 cycles, Y2Q1)
  (iii) low self-discharge rate (<0.5% per day, Y2Q2) during resting
  (iv) longest shelf-life of over one year (Y2Q2)
  All examined cells were fabricated with high-loading sulfur cathodes (70 wt.% and 4.0 mg cm^{-2} sulfur, Y2Q3, Y2Q4)

- The understanding gained is leading to the following (Y2Q3, Y2Q4):
  (i) advanced cathode design with high sulfur loadings of 30 ~ 60 mg cm^{-2} and with sulfur contents of 67 – 80wt.%
  (ii) cathode designs with low electrolyte/sulfur ratios of 6.8